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Direct Separation of Short Range Order in Intermixed Nanocrystalline and Amorphous Phases

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Using intense x-rays produced at beam line X16C of the National Synchrotron Light Source at Brookhaven National Laboratory, scientists have developed a new method to determine the regularity in the arrangement of atoms, called short-range order, in heterogeneous mixtures of the same chemical element in amorphous and nanocrystalline states. The method combines two synchrotron techniques, X-ray Absorption Fine Structure (XAFS) and Diffraction Anomalous Fine Structure (DAFS). For a sample containing amorphous and nanocrystalline germanium supported by a silicon dioxide matrix, the XAFS-DAFS combination allowed the scientists to separately analyze the short-range order of the germanium atoms.

Crystallization of amorphous materials and glasses is used to create commercial compact discs (CDs) and digital versatile disks (DVDs). The crystallization and amorphization rates can be increased, leading to faster and denser optical recording, by understanding how atoms interact within the material. Other possible applications resulting from this knowledge include studies of materials such as quantum dots, which are collections of between 100 and 1000 atoms, ion-damaged materials, and thin-film oxides.

We studied the local structure of a sample containing amorphous and crystalline germanium supported by a silicon dioxide matrix. The sample was annealed – heated and then slowly cooled down – , leading to the formation of tiny, roughly spherical crystals, or nanocrystals, about 15 to 20 nanometers (one nanometer is a billionth of a meter) in size (**figure 1**).

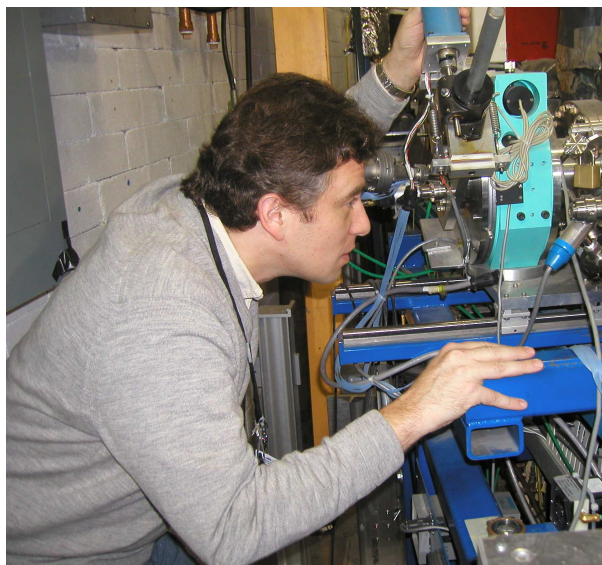
In this sample, three phases: amorphous germanium, nanocrystalline germanium, as well as a

fraction of germanium oxide, co-existed in small regions, each several tens of nanometers in size, within the silicon dioxide host matrix. The structural analysis of these regions was particularly challenging, because of their small size, the heterogeneity of the mixture inside the region, and the interfacial disorder between the three phases.

Due to the absence of the long-range order – the existence of a pattern that is regularly repeated – in an amorphous phase, x-ray

absorption fine structure (XAFS) is the technique usually used to solve the local structure in the amorphous germanium. In this technique, x-rays are projected onto the sample, and the ratio of absorbed photons versus total incident photons is measured at different x-ray energies to determine the nature and structure of the atoms in the sample. But because nanocrystalline germanium and germanium-oxide are also present in the sample, the XAFS signal is averaged over all germanium atoms.

Therefore, to disentangle the *local structures* of the amorphous and nanocrystalline germanium phases, as well as the germanium-oxide phase from the *average* structure around germanium atoms, it is essential to measure a partial XAFS signal from germanium atoms in the nanocrystalline phase. Then, co-refinement of the two XAFS signals, the one pertaining to the average germanium and the one related to the nanocrystalline germanium phase, would provide information on the short range order – regu-



Anatoly Frenkel at NSLS beamline X16C.

larity in the arrangement of atoms relative to their close neighboring atoms – of germanium in all three phases.

A technique serving this purpose is called the Diffraction Anomalous Fine Structure (DAFS). It is a hybrid of x-ray diffraction (XRD), in which x-rays are scattered by the atoms of an *ordered* phase, and XAFS, where the x-rays probe the *local* structure around specific type of atoms only. Thus, by using DAFS, it is possible to *selectively* probe the structure of nanocrystals and completely ignore the other phases in the sample (**figure 2**).

The XRD, XAFS and DAFS measurements were performed using a custom-designed diffraction instrument, or diffractometer, at beam line X16C of the National Synchrotron Light Source at Brookhaven National Laboratory. From the co-refinement of nanocrystalline germanium XAFS and the average germanium XAFS data, the mixing fractions and the nearest neighbor bond distances in all three phases were obtained. Interestingly, we found that the germanium-germanium distance in the amorphous germanium phase is three percent longer than that in the nanocrystalline germanium

phase. We believe that this difference is due to the large contribution of long germanium-germanium bonds located within the distorted amorphous-nanocrystalline interface layers.

This work illustrates that a combination of the DAFS and XAFS techniques can be used to determine the short-range order around a single atomic type in a sample of mixed ordered and disordered phases.

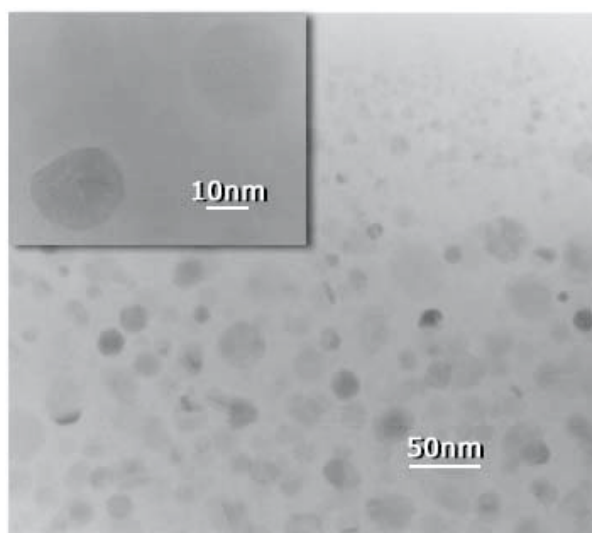


Figure 1. Image obtained by a transmission electron microscope of a sample of germanium nanocrystallites embedded in silicon dioxide.

Figure 2. (Top curve): Experimental (red dots) and theoretical (solid, black) signals for germanium-oxide phase and the averaged nanocrystalline and amorphous germanium phase.

(Bottom curve): Experimental (green dots) and theoretical (solid, black) signals by using the diffraction anomalous fine structure (DAFS) technique, showing that the contribution of the nanocrystalline phase is separated from the averaged nanocrystalline and amorphous phase.

